APPLICATION OF DGT SAMPLERS IN MONITORING OF MINE WATERS OF THE WITWATERSRAND GOLDFIELDS, RSA

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ABSTRACT

Passive sampling techniques are known to be very accurate for measuring dissolved and bio-available trace metals at a controlled rate because chemicals can accumulate continuously from water and concentrations of pollutants are time averarged (TWA) over the exposure period based on Ficks first law of diffusion. Diffusive Gradient in Thin-films (DGT) is a passive sampling technique, which has been successfully applied in a variety of environmental monitoring projects related to hazardous radionuclides, trace metals, organic contaminants and pharmaceuticals to precisely measure chemical releases. A DGT sampler is a very simple kit with a 25 mm diameter plastic backing cylinder and a front cap with a window of 20 mm in diameter.

A pilot scale DTG deployment was implemented in Central Witwatersrand sites, South Africa, where there are evidences of widespread environmental degradations. The results portray that some of the most critical chemical species are either undetected or measured orders of magnitude more with conventional grab samples than DGT samples. Furthermore, DGT samplers deployed along upper, middle and lower reaches of a local stream (Elsburg stream) help to identify the pollution source and evaluate evolution of chemical species along the stream length. DGT samplers deployed in five test pits at different depth around a slime dam near Delmore Village (East of Germiston Town) show that liming and trenching failed to contain deep seepage of critical pollutants from the source. The result highlights the considerable potential of using DGT samplers as a monitoring tool for evaluating the success of current short- and medium-term contaminant containment methods such as trenching.

1. GENERAL

Witwatersrand Gold Mining Businesses have been active for over one hundred years, where some of the mines in that region represent one of the earliest in South Africa (Bernand, 1999). After more than a century of mining with most in the basin being in a state of closure because of resource dwindling, the substantial multi-faced impacts of mining on the ecosystem (soil, landform, groundwater and surface water regime, biota) started to be felt on a significant scale. These impacts include, among other issues, surface/groundwater pollution, flooding of the mining basins with groundwater and stability problems, and the consequences of the afore-mentioned entities on the ecosystem.

Previous pollution assessments are based on data generated from samples taken using the conventional grab sampling method, which may not accurately represent the real chemical bioavailability of the whole media. Any interpretation and conclusion based on total concentrations regarded as effective concentrations is inaccurate and does not represent the real situation. The current project, through a co-operation between the Norwegian Institute for Water Research (NIVA) and the Council for Geoscience, was initiated to apply diffuse gradient in thin films (DGT) technology into the Witwatersrand mining district as part of Witwatersrand Central Basin Mine Water Apportionment Pilot Study Program.

2. INTRODUCTION

DGT is a passive sampling technique, which has been successfully applied in a variety of environmental monitoring projects related to hazardous radionuclides, trace metals, organic contaminants and pharmaceuticals to precisely measure chemical release at a controlled rate (Pierzynski et al., 2005). Mobility of selected chemical species (Cd, Zn and Pb) in rhizosphere was successfully assessed in the Czeck Republic with DGT samplers (Fischernova et al., 2005). DGT samplers were also deployed to assess pollution of Aluminum to fish population in Norway and determine the source of elevated the metal successfully (Lia et al., 2006, Royset et. al., 2005). Since the inception of use DGT samplers, several applications of the samplers help solve what has been a tedious and high uncertainty sampling method in Australia and U.S.A. (Larnera, and Seena, 2005). The application of DGT samplers is currently focusing towards standardization through research institutes (Lancaster University) and the International Network of Acid Prevention (INAP) while currently researches are on-going to manufacture advanced membranes (Zhao et al., 2002) at different conditions.

A DGT sampler is a very simple kit with a 25 mm diameter plastic backing cylinder and a front cap with a window of 20 mm in diameter (Fig. 1a). A layer of resin gel is placed on the base with side containing the resin facing upward acting as diffusion layer of hydrogel overlying a chelating resin below a filer membrane is used to facilitate diffusion of the chemicals over a period of time. (Fig. 1b).

Collectively the hydrogel and the filter membrane are known as the diffusion layer. The metal, released over a period of time, based on rate of dissociation, is measured by analyzing the chelex layer. In other words, organically or inorganically complexed metals have to dissociate during transport through the diffusive layer and time averaged. The DTG technique is superior to other sampling methods in that it accumulates chemicals continuously from water and can provide time weighted average (TWA) concentrations of pollutants over the exposure period based on Ficks first law of diffusion (Equation 1).

$$J = D \frac{dC}{dX}, \qquad \text{Equation 1}$$

where D is the diffusion coefficient (cm^2S^{-1}) and $\frac{dC}{dX}$ is the change in concentration gradient ($mol\ cm^{-4}$).

Figure 1a. DGT sampler

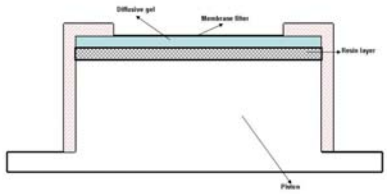

Figure 1b. Section of DGT sampler

DGT samplers are simple to install and easy to operate with a reasonable cost. Detail installation, deployment, storage, calibration and other procedures can be referred elsewhere (Zhang, 2002). DGT samplers measure *insitu* labile metal fractions which are bio-available (effective concentration) including flux making it a powerful tool for speciation calculation and for determination of rates of dissociations of metals.

3. THE STUDY AREA

The Central Witwatersrand Goldfield is located south of Johannesburg city, Guateng province, South Africa. The site one of the oldest goldfields in the country and in the world, giving the City of Johannesburg the name “City of Gold” (Figure 2). Because of the complex nature and long history of mining in Witwatersrand Goldfields which caused widespread pollution, there is a need to evaluate and assess regional geochemistry comprehensively in order to get a handle on rate and quantity of acid mine drainage generated from abandoned and active mines besides the mine waste dumps. Monitoring of mine drainages has been undertaken by using the conventional grab sampling of surface waters and ground waters from boreholes and surface water bodies respectively. Analytical data from samples taken using the conventional grab sampling method experience a high level of uncertainty owing to the experience level of the sampler, sample storage, the magnitude of concentration as not being time averaged, and not necessarily representing the labile or bio-availability of the chemical species. To date, the application of passive sampling using DTG samplers has never been utilized in South Africa, where there are several currently operating and abandoned mines throughout the country left and leaving a complex legacy of environmental pollutions.

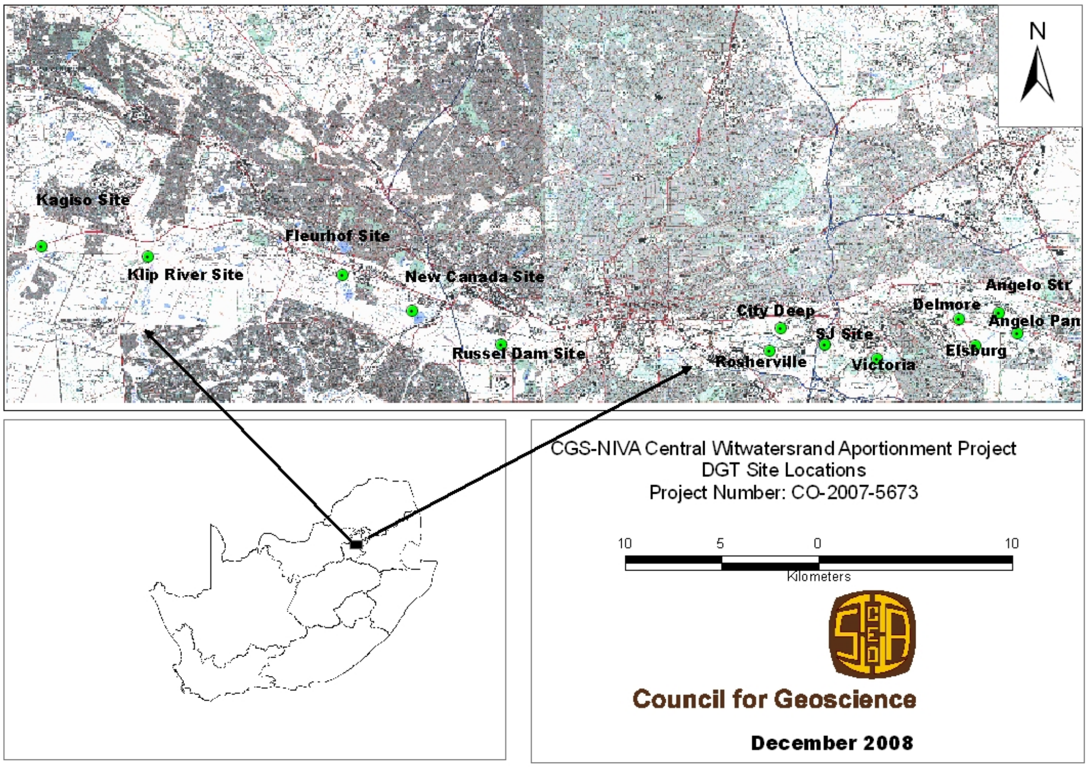

Figure 2. Sample locations in the Central Witwatersrand Goldfields

4. MATERIALS AND METHOD

DGT sampler kits and the gel chilex-100 and Whatman P-81 membranes were purchased from DGT research Ltd. (Lancaster, UK). DGT samplers were collected within a period of three up to 31 days after deployment in chosen streams, reservoirs, evaporation dams, slimes dams and boreholes. The samplers were put into water tight zip-locked bags which then was put in cooler box with ice cubes. Upon arrival at the CGS premise, the samplers were disassembled in an attempt to take out the inner membrane below the chilex and filter. The inner membrane was acid bathed in one millimeter of concentrated nitric acid for an overnight on a shaker to elute metals. It was investigated that concentrated nitric acid show an elution capacity of up to 95% (Royset et al., 2005). The samples were then diluted to 10% for another day to make them ready for analyses. Samplers in an ultra pure water was used as a blank and water samples using the conventional grab sampling was taken in selected sites for comparison purpose.

Temperature corrected diffusion coefficients of metal species, thickness of the filter membrane and the diffusive layer, DGT exposure area, time of deployment were used to calculate the uptake rate. Using mass of gel layer metal accumulation which is calculated from the analytical values, the final concentration calculated by dividing it with the flux per unit time.

5. RESULT AND DISCUSSION

Duration of Deployment

Two DGT samplers were deployed for a period of 3 and 31 days to assess the effect of deployment time on the final concentration. Although the borehole is situated downstream of a number dams, it seems that the borehole doesn’t have substantial pollution except for Fe and Mn. The result shows that the long-term deployment is one or two orders of magnitude of reduction in concentration than that of the short-term one for all chemical species (Figure 3). However, previous researches portray a more or less similar uptake rates for up to 48 hours beyond which the long-term deployments show a slightly decreased uptake for few species (Royset, 2002). The high discrepancy of the long and short term deployment is probably related to the excessive number of days of deployment (31 days).

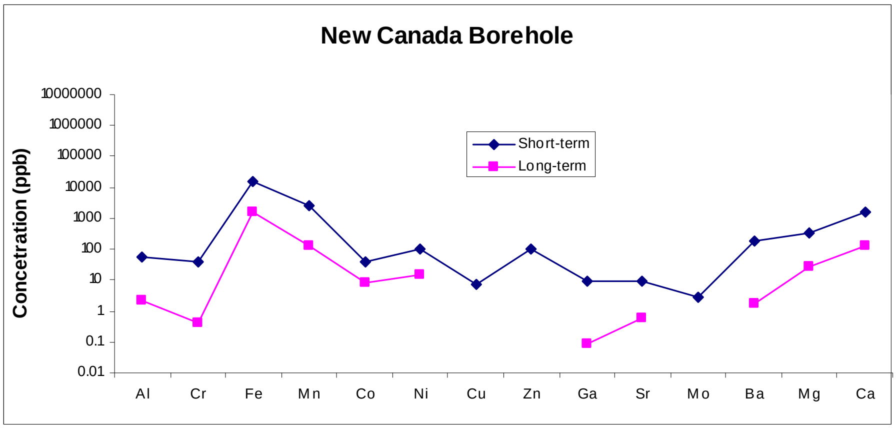

Figure 3. Calculated concentration of DGT samplers deployed in a borehole

Comparison of Data from DGT Versus Grab Sampling

It is observed that conventional grab sampling data are higher by up to one order of magnitude than the corresponding concentration data of DGTs (Figure 4). The discrepancy is consistent for all chemical species but grab samples have not captured some chemical species of concern (Pb, U, Cd). The result highlights that DGT's subdued uptake of earth alkali metals in almost all samples (Figure 4).

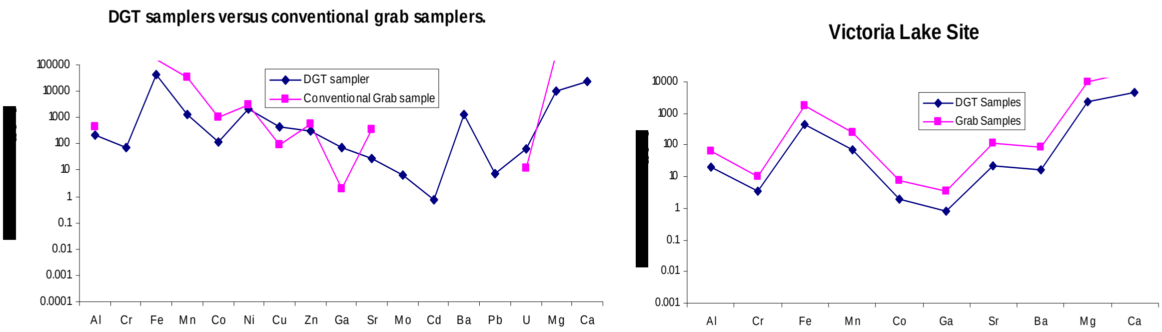

Figure 4. Comparison of concentrations between DGT and conventional grab samples

DGT Samplers in Assessing Stream Pollution

A number of DGT samplers were deployed along the upper, middle and lower reaches of the Elsburg stream in the Central Witwatersrand area, south east of Johannesburg in the vicinity of Germiston town to assess the evolution of metal pollution along the route (Figure 5). The site was chosen because of its downstream location of a number of slimes dams, waste rock damps, landfill and other pollution sources.

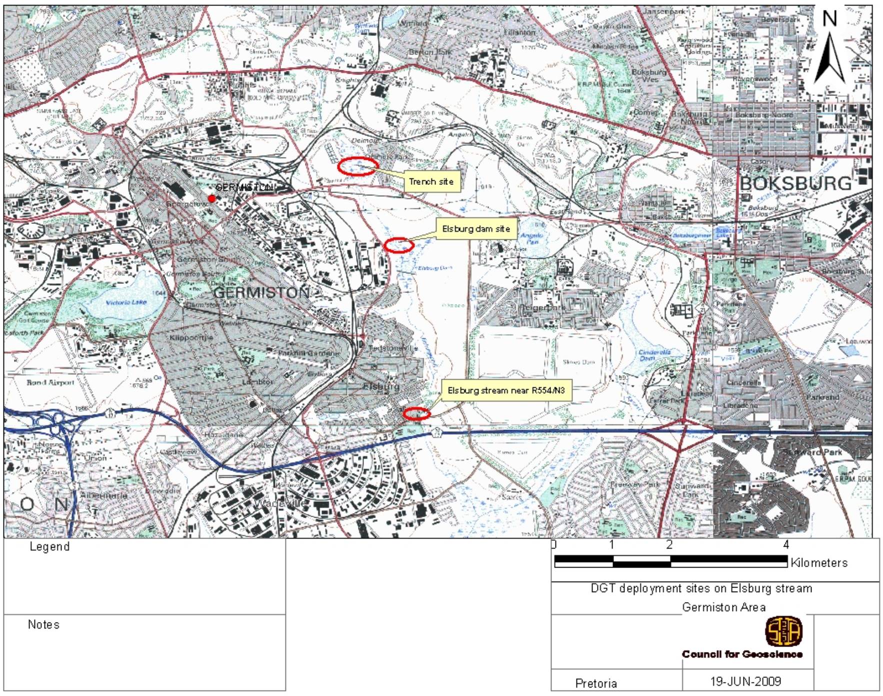

Figure 5. Sample location along the Elsburg stream

Most metal species depict that, except U and Al, which shows higher value in the upstream of the stream, there are no clear trend as to whether or not some contaminants are up taken, and complexed along the way (Figure 6). The absence of trend may indicate that there are more than one sources along the path of the stream. Nevertheless, with proper selection of sampling sites and dense sampling points, there is a potential to apply DGT sampling for stream water quality assessment conveniently and with lower cost.

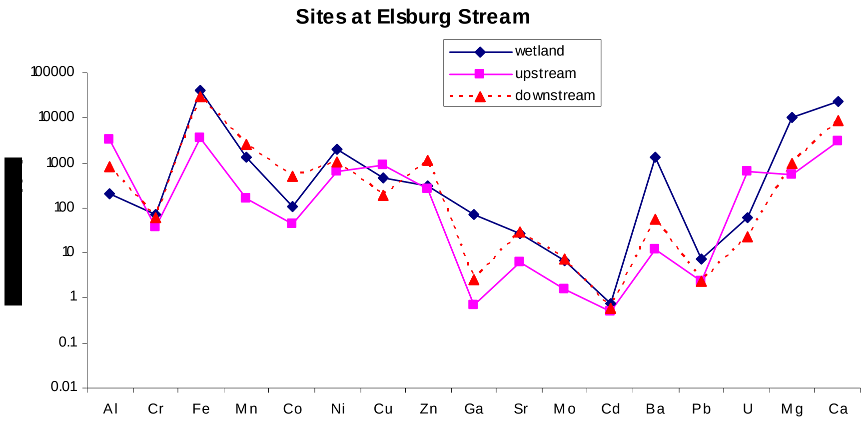

Figure 6. DGT analytical data along the Elsburg stream

DGT Samplers in Slime Dam Site Monitoring

In Central Witwatersrand goldfields trench construction around slimes dams has been done as a tool to prevent and manage mine drainages from polluting surface water bodies. In an effort to assess the effectiveness of such trenches, five shallow augers (1.5 m to 20 m), strategically positioned around a slime dam, were drilled where DGT samplers were placed. A wetland, presumably generated by the seepage of the slime dam, is sited immediately east of the slime dam. The data of surface trench consistently indicate slightly higher concentration of all but Ni and Co. However, considerably high concentration of the majority of deleterious metals species were detected up to a depth of 20 m (Figure 7).

The result underscores the fact that liming and trenching are not effective in containing vertical contaminant movements. Moreover, the result stresses the potential of using passive samplers (DGT) to monitor the effectiveness of existing pollution control methods.

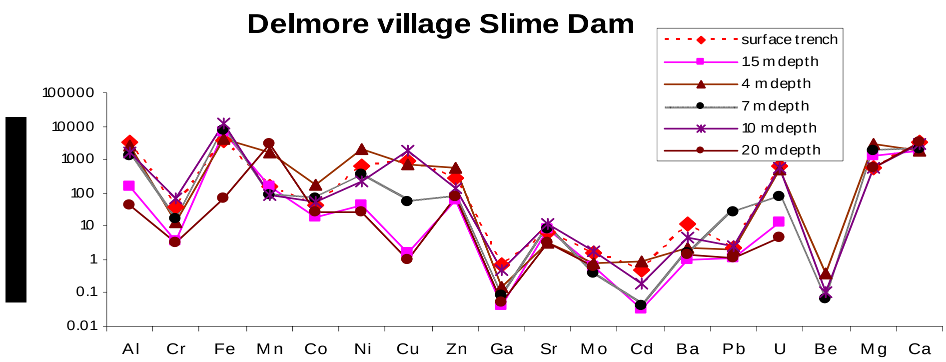

Figure 7. DGT data at different depths.

6. SUMMARY AND CONCLUSIONS

Passive samplers are superior to the conventional grab sampling in accurately measuring labile metals which are bio-available, averaged over a certain period of time. Errors associated with sample storage and experience of the sampler can be reduced to an acceptable level with passive samplers. It is possible to precisely calculate free ion activity by using different diffusive layers to trap inorganic and organic species separately.

DGT samplers show a considerable potential in monitoring mine related water pollution accurately and with lower costs. In the central Witwatersrand goldfields, DGT samplers allow accurate determination of bio-available metal species, which may not be detected or measured in a higher magnitude by the conventional grab samplers. Total concentrations determined from grab samples does not necessarily represent the amount of harmful metal available to organisms.

DGT samplers show a great potential to supervise evolution of metal species along polluted streams and perhaps determine the source of pollution. The concentration data helps design effective stream pollution management schemes.

Monitoring of acid mine generation control schemes can be implemented by using DGT samplers. Because of deployment ease and relatively low installation cost, DGT samplers can be deployed at chosen depths and locations to examine the risk of pollution to surface and groundwater resources which are vital supply of water to the community.

7. ACKNOWLEDGEMENT

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8. REFERENCES

Bernand H., 1999
Hydrogeology Map (1:500,000) of the Johannesburg Area
Fischernova, Z., Szakova, J. and Pavlikova, T.
The Application of Diffusive Gradient in thin films (DGT) for assessment of changes in Cd, Zn and Pb mobility in Rhizosphere, *Plant Soil Environ., 51, 2005 (12); 532 - 538*
International Network for Acid Prevention (INAP), 2003
A technique for determining Bio-available metal concentrations
Lia, W., Zhao, J., Chunsheng L., Kisera, S. and Cornetta, R.
Speciation measurements of uranium in alkaline waters using diffusive gradients in thin films technique, *River water Analytica Chimica Acta, Volume 575, Issue 2, 11 August 2006, Pages 274*-280
Larnera, B. and Seena, A.
School of Chemistry, University of Tasmania, Locked Bag 1371, Launceston, Tasmania 7250, Australia, *Analytica Chimica Acta. Volume 539, Issues 1-2, 10 May 2005, Pages 349-355*
Pierzynski, M. , Michael J. , Schneegurt, M., 2005
Evaluation of Chemical and Biological Assays as Indicators of Toxic Metal Bioavailability in Soils
Røyset, O., BO Rosseland, T Kristensen, F Kroglund, Ø Å Garmo, E Steinnes, (2005) Diffusive Gradients in Thin Films Sampler Predicts Stress in Brown Trout (Salmo trutta L.) Exposed to Aluminum in Acid Fresh Waters, *Environ. Sci. Technol. 2005, 39, 1167-1174.*
Røyset, O., Aaberg, O. and Stennes, E. (2002)
RAPPORT LNR 4604-2002, Performance study of diffusive gradients in thin films (DGT) for 55 elements. On line Publication, *American Chemical Society, Analytical Chemistry, 1 - 8*
Zhang, H.
DGT Research Limited, Skelmorlie, Lancaster, Quernmore, LA2 AQJ UK

Zhao, W., Teasdale, P., John, R. and Zhang, S.
Application of cellulose ion exchange membrane as a binding phase in the diffusive gradient in thin films technique for measurement of trace metals, *Analytica Chemical Acta 464, 2002, 330 – 339*.